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ALKALI-STABLE, SURFACE-ACTIVE, ANTI-FOAMING AGENTS (ACETALS)
[Alkalistabile, oberflächenaktive, schaumdämpfende Mittel (Acetale)]

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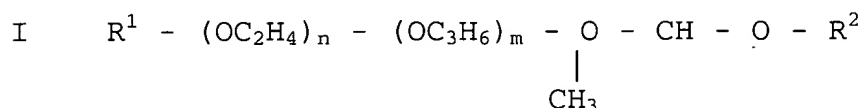
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The invention relates to compounds of Formula I

/1*



in which R^1 is a straight-chained or branched saturated or unsaturated alkyl residue with 7 to 22 carbon atoms, or a mononuclear or binuclear alky aryl residue with 8 to 12 carbon atoms in the alkyl chain; R^2 is a straight-chained or branched alkyl residue with 1 to 10 carbon atoms, a cyclohexyl residue which, possibly, is alkyl-substituted, or a residue of the formula $(\text{C}_3\text{H}_6\text{O})_m - (\text{C}_2\text{H}_4\text{O})_n - \text{R}^1$, n is an integer number from 1 to 30, and m is an integer number from 5 to 50 with the proviso that, the ratio of m to n , is, at least, 1 : 1.

Although polyoxyalkylated phenols and polyoxalkylated aliphatic alcohols represent appropriate non-ionic tensides, they are not suitable for use in technical cleaner formulations because the presence of alkaline substances is required in them. Polyoxalkylated aliphatic alcohols or alkyl phenols are easily oxidatively degraded in the presence of strongly alkaline reactive compounds, such as caustic alkali or soda, which results in degradations and discolorations.

It is known to the art that the free terminal hydroxyl groups of polyoxyalkylated alcohols or phenols can be converted with reactive groups, in order to obtain stable polyethers. Thus, this doctrine is the subject of the German laid-open specifications 1520647 where polyoxethylated alcohols or alkyl phenols are converted with olefins

*Number in the margin indicates pagination in the foreign text.

in such a way that the terminal groups, i.e., the free hydroxyl groups, are sealed.

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Symmetrically terminal group-sealed polyglycolic ethers are described in the American patent document 2905721 which remain preserved through a bilateral conversion of polyglycolic ethers on the basis of ethylene oxide with higher vinyl ethers. These compounds are described as raw materials for fine low-foaming cleaning agents in this literary source.

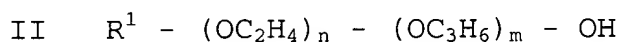
In spite of very good wetting properties of these products, the low-foaming characteristics of these products still leaves a lot to be desired. During automatic dish-washing, too little water is taken to the surfaces to be cleaned if high-foaming detergent formulations are used, and the mechanical support of the wash effect is inhibited by the moving parts of the machine.

It is known to the art that, apart from compounds, such as ethers, etc., acetals and ketals are also highly stable compared to alkalis. If the known, above-specified polyoxalkylated alcohols or alkyl phenols are added to vinyl ethers, mixed and symmetrical acetals of these polyoxalkylated alcohols or phenols are obtained under certain prerequisites.

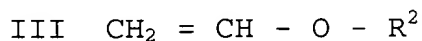
In a surprising manner, the compounds of Formula I have now proved to have superior alkali-stable tensides with substantially improved anti-foaming properties while simultaneously maintaining high cleaning power and biodegradability.

Not last, the excellent anti-foaming effect of the compounds in accordance with the invention is realized on account of the propylene oxide-ethylene oxide ratio of, at least, 1:1, in contrast to which, a higher ethylene oxide percentage has always been desired in comparison with more dated patent specifications with these kinds of oxylates (ratio, at least, 3:2), in order to leave a sufficiently high percentage of hydrophilic groups in the molecule.

The preparation of the new acetals of Formula I is simple and is /3 carried out in the manner that, a polyoxalkylated alcohol of the Formula II



is converted with a vinyl ether of the Formula III



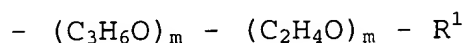
in the presence of acidic catalysts. In the Formulas II and III, R^1 , R^2 , n , and m , have the same meaning as in Formula I.

Lewis acids, such as BF_3 , AlCl_3 , TiCl_4 , or mineral acids, such as HCl , H_3PO_4 , H_2SO_4 , or HClO_4 , are particularly appropriate as catalysts.

Even strong organic acids, such as methane sulfonic acid, propane sulfonic acid, trinitrobenzene sulfonic acid, p-toluene sulfonic acid, trifluoromethane sulfonic acid, or trifluoroacetic acid, catalyze the conversion of the polyoxalkylated alcohols or phenols with vinyl ethers extremely well.

Expediently, the reaction can be carried out at temperatures from 0 to 100°C . Generally, if temperatures of $< 30^\circ\text{C}$ are selected, compounds

of Formula I are created in which R^2 stands for alkyl residues or cycloalkyl residues of the specified definition, in contrast to which, at temperatures of over 30°C, compounds are created with increasing temperatures in which R^2 stands for the residue



If compounds with a low turbidity point are desired, the work is expediently carried out at higher temperatures.

However, preferably, the work is conducted at the lower temperatures because the most favorable compounds result in this way from the perspective of application technology.

Long-chained alcohols with 7 to 22 carbon atoms are options as original substances. These may be saturated or unsaturated and /4
unbranched or branched and include all alcohols of the mentioned carbon numbers, or their mixtures. Preferably, alcohol mixtures are used, such as those which can be obtained from Ziegler or crack olefins through oxosynthesis. Alcohol fractions which are especially preferred, for instance, include the C_{12} - C_{15} - or C_{14} - C_{16} sections.

The known isomeric alkyl phenols or alkyl naphtols are additional original products, whereas the alkyl residues contain 8 to 12 carbon atoms.

Here, octyl phenol or nonyl phenols are of particular significance in the sense of the invention.

The substances mentioned, preferably, the C_9 to C_{16} alcohol fractions, are initially converted with 1 to 30 mol, preferably, 5 to 20 mol of ethylene oxide, and, subsequently, oxpropylated, whereas propylene oxide is used

to such an extent that the molar ratio of propylene oxide in relation to ethylene oxide is, at least, 1 : 1, however, preferably, 1.1 : 1 to 6 : 1. Expediently, 5 to 50 mol of propylene oxide, preferably, 10 to 25 mol, are used.

The oxethylation or subsequent oxpropylation is carried out in accordance with tried and tested methods in the presence of alkaline catalysts, such as KOH or NaOH, whereas the accumulation of ethylene oxide takes place at temperatures of, for instance, 130 to 160°C, and pressures of 0 to 5 atmosphere above atmospheric pressure, and the oxpropylation, for instance, takes place at temperatures from 110 to 130°C, and pressures from 0 to 10 atmosphere above atmospheric pressure.

Subsequently, the polyoxylated alcohols or phenols of the above definition are converted while using small quantities of strong inorganic or organic acids, or Lewis acids, as catalysts, with a vinyl ether of Formula III to compounds of Formula I. Because, to the extent possible, the conversion should be allowed to take place quantitatively, 2 to 3 mol of the vinyl ether of Formula III per free hydroxyl group are expediently used.

In Formulas I and III, R², preferably, is an alkyl residue with 1 /5 to 10 carbon atoms, or a, possibly, alkyl-substituted cyclohexyl residue, whereas, above all, 2-methyl- and 2-ethyl residues are options as alkyl substituents. For instance, preferred vinyl ethers of Formula III that are used in the spirit of the invention to prepare the compounds of Formula

I, include methyl vinyl ether, ethyl vinyl ether, isopropyl vinyl ether, n- and iso-butyl vinyl ether, as well as 2-methyl cyclohexyl vinyl ether.

The addition of the vinyl ethers should take place at the above-specified temperatures.

The compounds in accordance with the invention are suitable as formulations with solid sodium hydroxide or sodium metal silicate and tripolyphosphate etc. as low-foaming, alkali-stable industrial cleaners for all types of solid surfaces, for instance, as metal cleaners prior to plating, preparation and processing, or also as cleaners in automatic dish washers and bottle washers. Apart from 2 to 5 parts of these new tensides, detergent formulations of this kind contain 75 additional parts of solid sodium hydroxide, aside from 25 parts of sodium tripolyphosphate and sodium metal silicates as detergent filler substances.

With these formulations, no discoloration or degradation of the surface-active compounds which can easily be observed by means of a poorer foaming behavior, will occur even after a prolonged dwell period.

In other mixtures, the substances in accordance with the invention are also appropriate as wetting agents and cleaners for the treatment of textiles and the cleaning of all kinds of non-porous surfaces.

The products obtained in this manner proved to be detergent /6
tensides of excellent effectiveness with a fine surface and interfacial activity with low-foaming properties. The simultaneously excellent very good alkaline stability proved itself in the fine color stability in contact with strong alkali at normal and elevated temperatures over

extended periods of time. Under these chemical and thermal stresses, the interfacially active functions also remained virtually unchanged in the form of the measurable surface tension, wetting effect, and low amount of foam.

The following examples will explain the invention with regard to the preparation of compounds and with respect to their use as cleaners for solid surfaces. The stated parts and percentages relate to weight.

Example 1

3 to 4 parts of a 5 to 10% solution of boron fluoride etherate in diethylether are dripped into a mixture of 400 parts by weight of a conversion product of a C_{12} - C_{15} -oxoalcohol mixture with 5 mol of ethylene oxide and 15 mol of propylene oxide, and 72 parts by weight of ethyl vinyl ether which has been cooled to about 10°C . By cooling further, the reaction mixture is kept at 5 to 15°C by cooling further under agitation. After 2 to 3 hours, the temperature is allowed to slowly increase to room temperature, and, then, stirring continues for 1 to 2 hours.

Subsequently, the catalyst is removed by agitating with 2 parts of sodium carbonate for 30 minutes. After filtering off, the excessive ethyl vinyl ether, acetaldehyde diethyl acetal, as well as other volatile components, are withdrawn in a vacuum while gently heating to about 40°C under agitation. A limpid, light-colored product is obtained in a yield of 96 to 99%.

The created tenside, a mixture of symmetrical and asymmetrical acetal of the acetaldehyde with polyoxalkylated C₁₂-C₁₅ oxoalcohol and ethanol, is extremely low-foaming and possesses very good wetting capabilities (see Table) with an extremely high alkali stability. /7

The compounds listed in Table 1, which were subsequently tested from an application technical viewpoint, were prepared in a similar manner.

Three different samples are consulted to test the alkali stability, in order to evaluate the behavior under various conditions:

Test 1: 45.00 g of sodium metal silicate pentahydrate are spread out in a flat porcelain dish of an approximate diameter of 15 cm in a thin, even layer. The dish is placed on a laboratory scale which weighs with an accuracy down to 0.01 g. Then, by means of a spray device, 5.00 g of the tenside to be tested are sprayed on the surface of the powder as evenly as possible. Subsequently, one mixes very thoroughly with a spatula without losing any substance, and, after a quantitative transfer into a mortar, the pestle is used for thorough trituration, in order to realize utmost homogeneity of the mixture.

An part of this mixture which is exactly aliquot in weight, e.g., one half, is weighed in a petri dish of 10 cm diameter, and evenly distributed in it in a thin layer. This part is described as portion A and stored in a heat cabinet in a normal atmosphere at 60°C for 40 days. The sample is taken out every 3 to 5 days and visually inspected for any changes in color. The aliquot rest of the whole mixture, called portion B, is consulted for the measurement of the initial value of the surface tension (10 g/l of distilled water, 20°C, tensometer according to Lecomte de Nouy) for the initial measurement of the foam volume in accordance with DIN 53902, page 1 (25°C, 20 g/l of distilled water), as well as for the storage sample at room temperature in a normal laboratory atmosphere (storage period of 40 days). The visual inspection for potential color changes is carried out in the same intervals as with portion A (see above).

The final samples with regard to surface tension and foam volume /8 are extracted from portion A after 40 days. In this process, the present weight of portion A must be accurately determined first, so that the aliquot weight percentage can be extracted for the measurement of the surface tension which, when the time in storage began, was 1.00 g if, e.g., 100 g of a 10 g/l solution are to be started. The same applies for the preparation of the 20 g/l solution for the foam test.

Test 2: 50 g of a 50% caustic soda solution are intensively mixed in a beaker glass with 0.5 g of the tenside which is to be tested, and, subsequently, they are transferred into a reagent vessel. The latter is kept in a heat cabinet at 60°C for 50 days without being locked. In

the heat, the tenside sediments on the surface of the fluid as a separate layer. Observations for changes in color are made at intervals of 3 to 5 days, both in the upper organic and in the lower aqueous-alkaline phase.

Test 3: 10 g of sodium hydroxide pellets are poured into a reagent vessel with 20 g of tenside at room temperature. The mixture remains exposed in the normal laboratory atmosphere at room temperature for 12 days. Observations for changes in color are made every other day, both in the upper organic fluid layer and in the interfacial layers of the sodium hydroxide pellets.

In products in accordance with Examples 2, 3, 5 to 13, 15, 17, and 18, no changes in color were observed in any of the 3 tests, even after dwelling for weeks.

The products in accordance with the Examples 4, 14, and 16, already began to yellow after 2 to 3 days, whereas the depth of color increased with time.

Table

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Beispiel	Ausgangsverb.	Mol (C ₂ H ₄ O)	Mol (C ₃ H ₆ O)	R ²	Trübkpt. (1% in 40% Bu. glyk.)	Oberfl. spannung (dyn cm ⁻¹)	Schaumverb. (10 Schlagmethode)		
							1 min	5 min	10 min
2	C ₉ -C ₁₁ -Oxoalk.	5	6	C ₂ H ₅	46.5	29.5	100	70	30
3	C ₉ -C ₁₁ -Oxoalk.	5	13	1-C ₄ H ₉	44.5	29.8	100	50	20
4	C ₁₂ -C ₁₅ -Oxoalk.	5	0	1-C ₄ H ₉	59.6 (in H ₂ O)	24.9	480	100	70
5	" " "	5	6	CH ₃	45.9	30.1	50	20	5
6	" " "	5	6	C ₂ H ₅	46.3	30.9	9	5	0
7	" " "	5	6	1-C ₄ H ₉	43.7	30.4	10	5	0
8	" " "	5	13	CH ₃	46.4	30.5	0	0	0
9	" " "	5	13	C ₂ H ₅	49.9	31.4	10	8	0

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Beispiel	Ausgangsverb.	Mol (C ₂ H ₄ O)	Mol (C ₃ H ₆ O)	R ²	Trübpt. (1% in 40% Bu.glyk.)	Oberfl. spannung (dyn cm ⁻¹)	Schaumverh. IG Schlegelmethode)		
							1 min	5 min	10 min
10	C ₁₂ -C ₁₅ -Oxoalk.	5	13	C ₃ H ₇	45.8	31.0	15	10	5
11	C ₁₂ -C ₁₅ -Oxoalk.	5	13	1-C ₄ H ₉	43.7	30.5	5	0	0
12	Alfol.20+R	6	14	C ₂ H ₅	49.8	31.1	10	0	0
13	Alfol.20+R	6	14	1-C ₄ H ₉	46.5	30.8	5	0	0
14	Octylphenol	10	0	C ₂ H ₅	50.2	30.5	600	300	200
15	Octylphenol	5	10	1-C ₄ H ₉	49.1	30.0	20	10	5
16	Nonylphenol	10	0	1-C ₄ H ₉	43.9	29.7	500	400	200
17	Nonylphenol	10	10	C ₂ H ₅	40.5	29.9	170	100	50
18	Nonylphenol	5	10	C ₂ H ₅	40.8	30.5	100	50	10

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Table

Key:

Beispiel = example

Ausgangsverb. = original compound

Trübungspunkt = turbidity point

Oberfl. spannung = surface tension

Schaumverh. = foaming behavior

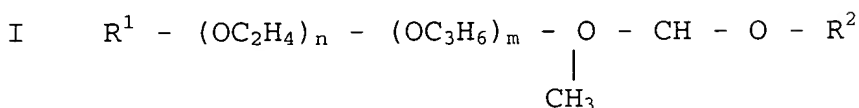
IG Schlagmethode = IG beating method

Forts. Tabelle = Table continued

Patent Claims

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1. Compounds of Formula I



in which R^1 is a straight-chained or branched saturated or unsaturated alkyl residue with 7 to 22 carbon atoms or a mononuclear or binuclear alky aryl residue with 8 to 12 carbon atoms in the alkyl chain; R^2 is a straight-chained or branched alkyl residue with 1 to 10 carbon atoms, a cyclohexyl residue which, possibly, is alkyl-substituted, or a residue of the formula $(\text{C}_3\text{H}_6\text{O})_m - (\text{C}_2\text{H}_4\text{O})_n - \text{R}^1$, n is an integer number from 1 to 30, and m is an integer number from 5 to 50 with the proviso that, the ratio of m to n , is, at least, 1 : 1.

2. Industrial cleaner or detergent containing, at least, one compound in accordance with Claim 1.